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ANOMALOUS SURFACE PHASE FORMATION ON Pt_3Sn <110>

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Abstract. LEED analysis of the clean annealed surface of a <110> oriented Pt_3Sn single crystal surface indicates the formation of a multilayer surface phase which does not have the Ll_2 bulk structure. LEISS analysis indicates a surface stoichiometry of ca. 1:1 with Sn atoms displaced ca. 1.4 above the plane of Pt atoms. The surface phase is hypothesized to be a rhombic distortion of the <0001> plane of PtSn, which has a $B8_1$ (NiAs-type) bulk structure. It is not clear whether the phase forms by precipitation of PtSn due to a slight (0.5%) stoichiometric excess of Sn in the bulk, or due to multilayer reconstruction driven by surface segregation.

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1. Introduction

Pt-Sn alloys are of considerable commercial interest as both heterogeneous catalysts for hydrocarbon conversion [1-2] and as electrocatalysts for the direct electro-oxidation of methanol in fuel cells [3-4]. Of particular fundamental interest is the behavior of the highly ordered exothermic alloy Pt_3Sn [5]. Experimental studies of polycrystalline Pt_3Sn [6-8] found surface enrichment in Sn by LEISS, with surface compositions as high as 50-60 at. % Sn. To date we are not aware of any experimental study of the surface structure and composition of a Pt_3Sn single crystal.

The ordered Pt_3Sn alloy has the $Cu_3Au(L1_2)$ structure with tin atoms on the corners of the face centered cubic unit cell. Other members of the $L1_2$ family (Cu_3Au [9-11], Ni_3Al [12-13], and Pt_3Ti [14]) have bulk termination of the <111> and <100> single crystals, with the minority atom positioned slightly upward from the plane of the majority atoms [12-13,15]. If Pt_3Sn single crystal were to behave similarly, one would also expect the <111> and <100> surfaces to be bulk-terminated with a slight displacement of the Sn atoms upward from the plane of Pt atoms. However, because of the surface enrichment of Sn observed on polycrystalline Pt_3Sn, it is not obvious that the Pt_3Sn single crystal samples would behave like Cu_3Au and Ni_3Al. In another paper [16], we report results on the surface structure and composition of <111> and <100> oriented single crystals of Pt_3Sn using LEED, AES, and LEISS. We found that the Sn atoms are in p(2x2) and c(2x2) arrays on the <111> and <100> crystals, respectively, but are displaced upward from the plane of Pt atoms. In this paper, we report the first study of the surface structure and composition of the <110> oriented single crystal

of Pt_3Sn using the same combination of techniques. For this surface, we found an unusual form of surface reconstruction with Sn atoms raised above the plane of Pt atoms. However, unlike the <111> and <100> surfaces, which still have Sn atoms in $L1_2$ lattice positions, the Sn atoms appear to occupy lattice positions related to the $B8_1$ (NiAs-type) structure of PtSn.

2. Experimental

The apparatus and procedures for analysis of the <110> crystal is reported elsewhere [16]. For LEISS analysis, the angle of incidence of the ion beam with the surface normal could be varied continuously, but the azimuthal orientation could not. For these experiments, the 1 keV $^{20}Ne^+$ ion beam at glancing incidence was aligned along the <002> direction of the crystal and the scattering angle fixed at 135°.

Results

A poorly defined (110)-(3x1) pattern (Fig. 1a) was observed after Ar^+ ion bombardment and low temperature annealing. The (3x1) pattern was associated with a low Sn/Pt AES ratio which we attribute to the reconstruction [17] of a nearly-pure Pt (110) surface. Further annealing of this surface at higher temperature produced a diffuse (1x2) pattern (Fig. 1b), a transition through a sharper but streaked (1x2) co-existing with a rhombic pattern shown in Fig. 1c. The pattern is commensurate, having the structure given in matrix notation as

$$\begin{matrix} 1 & 0 \\ 1/2 & 3/2 \end{matrix}$$

which we will refer to as the "rhombic" structure. One of the surprising aspects of the rhombic pattern is the disappearance of many of the fundamental beams from the (110) substrate, e.g. the (01), (02), (12), etc. (see Fig. 1d). The changes in LEED structure with annealing

were accompanied by concomitant increases in the Sn/Pt AES ratio (factor of four times higher after complete annealing). The absence of the fundamental beams means the structure associated with the rhombic pattern must be sufficiently thick to attenuate the substrate beams.

The LEISS spectra at normal incidence for all the clean annealed surfaces of all three low index surfaces are shown in Fig. 2. The Sn/Pt intensity ratios on the <110> and <100> surfaces are practically identical, and are about 2 times that for the <111> surface.

The variation of Sn/Pt LEISS intensities with the angle of incidence was similar to the variation we observed on the <100> surface [16]. There was little change between normal incidence and 45°, then rapid change between 45° and 25°, with Sn/Pt ratio increasing by a factor of 8-10 (see Fig. 3a for definition of angles). Below 15°, the Pt signal was completely attenuated. Such an angular variation is consistent with a structure with Sn atoms above the plane of Pt atoms, shadowing the Pt atoms in the plane below. A shadow cone analysis (Fig. 3b) of these intensity variations together with knowledge of the Sn-Sn spacing (from the LEED pattern) enabled us to determine the distance the Sn atoms were displaced above the Pt atom plane [16]. The separation between the Sn atom and the Pt atom planes for the rhombic structure on the <110> calculated from this analysis is ca. 1.4Å.

4. Discussion

Unlike Pt3Sn <111> and <100>, where tin surface segregation produced structures having the same symmetry as the bulk, the LEED pattern of the Pt3Sn <110> crystal surface does not have L12 symmetry. What was observed was a reconstructed surface *region* at least three atomic layers deep, with quasi-hexagonal (actually rhombic) symmetry and not the rectangular symmetry of either (110)-(1x1) or (110)-(2x1). The LEISS analyses indicate the composition of the <110> surface is the same as the <100> surface, i.e. 50% Sn. It is possible that the reconstruction is related to a surface phase of another bulk alloy phase, e.g. the PtSn phase. PtSn has the $B8_1$ or NiAs-type structure [18] and its heat of formation is even more exothermic than that of Pt_3Sn [19]. Bulk termination of this structure normal to <0001> produces a surface with hexagonal symmetry. A rhombic distortion of this plane (ca. 5% contraction is one direction and 10% expansion in the other) would fit reasonably well onto the (110)-1x1 substrate, but this is the only reasonable match of any ordered Pt-Sn phase onto a fcc (110) lattice. The spacing between the Sn atom plane and the Pt atom plane in PtSn [18] agrees well with the interplanar spacing we found here by LEISS.

It is not clear why a new surface phase would form only on the <110> oriented crystal and not on either the <111> or <100> crystals. One obvious factor, which is difficult to eliminate *entirely*, is a shift difference in bulk composition between crystals, particularly a slight, e.g. 0.5%, *excess* of Sn in the <110> crystal. Given the bulk phase diagram of Pt-Sn [20] and the relative free energies of formation of PtSn and Pt_3Sn [19], *any* excess of Sn in the normally Pt_3Sn bulk crystal

could be expected to produce *precipitation* of a PtSn phase at the grain boundaries and/or free surfaces of the Pt_3Sn crystal, the total quantity/thickness of the precipitate being proportional to the amount of excess Sn. Analysis of all three crystals by emission spectroscopy (Galbraith Labs.) did not indicate any significant (<0.5%) difference in bulk composition between crystals, all being slightly *deficient* (0.5-0.8%) in Sn. However, we are continuing these analyses by other methods.

If, in fact, the surface phase forms on a Pt_3Sn bulk by reconstruction rather than by precipitation, it would be a unique form of multilayer reconstruction. Presumably the driving force for reconstruction is surface segregation of Sn [5], and the lower free energy of surfaces enriched in Sn. Why multilayer reconstruction is required to achieve the lowest energy state on the <110> surface, and not the <111> or <100> is puzzling.

Acknowledgments

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Figures

[1] LEED patterns (a-c) at 90 eV: a.) after ion bombardment, b.) after annealing at 500°C, c.) after annealing at 800°C, and d.) schematic of (c), where (x) is superimposed on LEED pattern for (110)-1x1 (o).

[2] Normal incidence LEIS spectra for all three crystal orientations.

[3] Off-normal incidence scattering geometry and Sn shadow cone geometry. N - surface normal, a - angle of incidence, a_e - angle of incidence for complete shadowing of the Pt plane, φ - scattering angle.

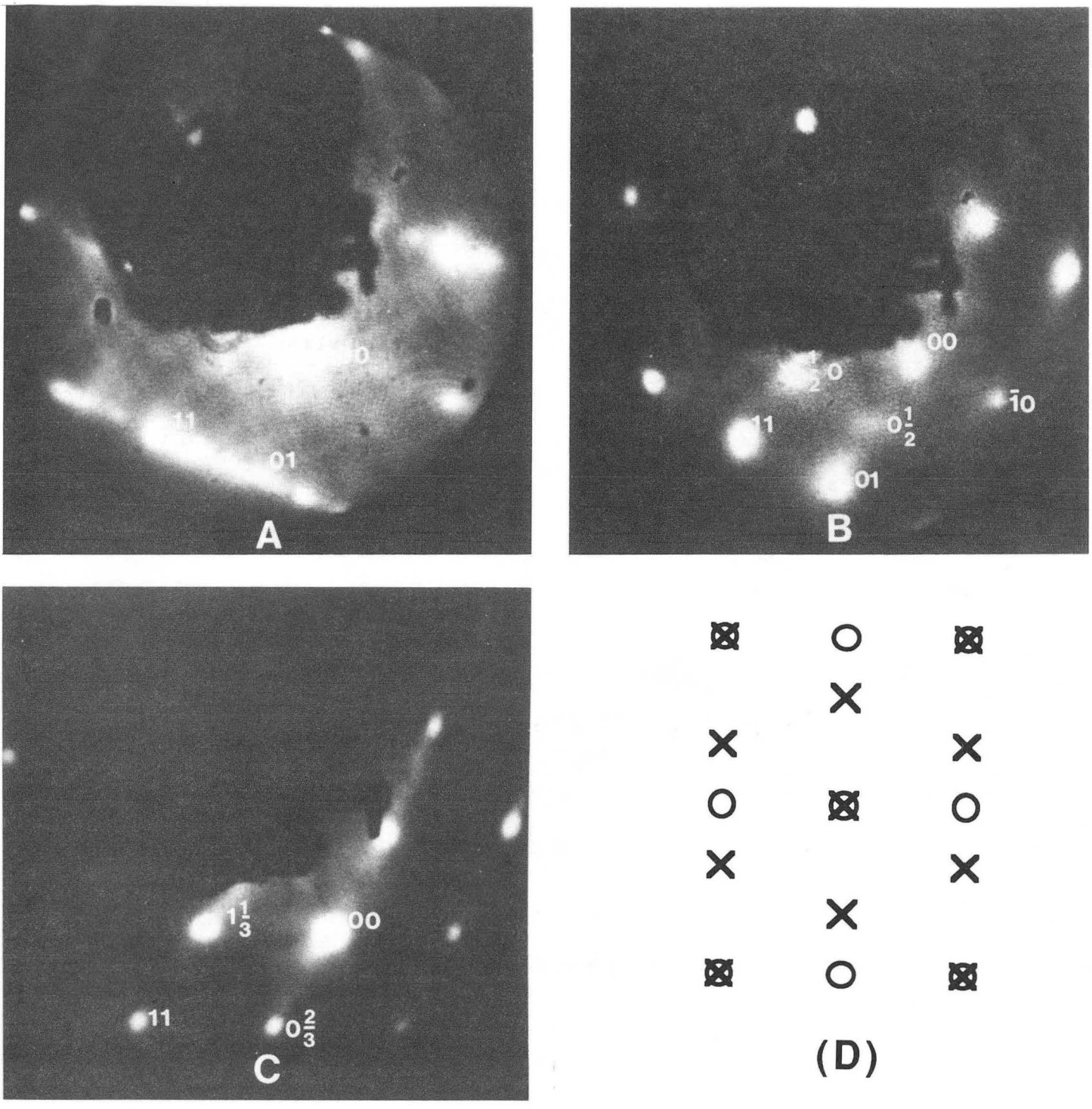
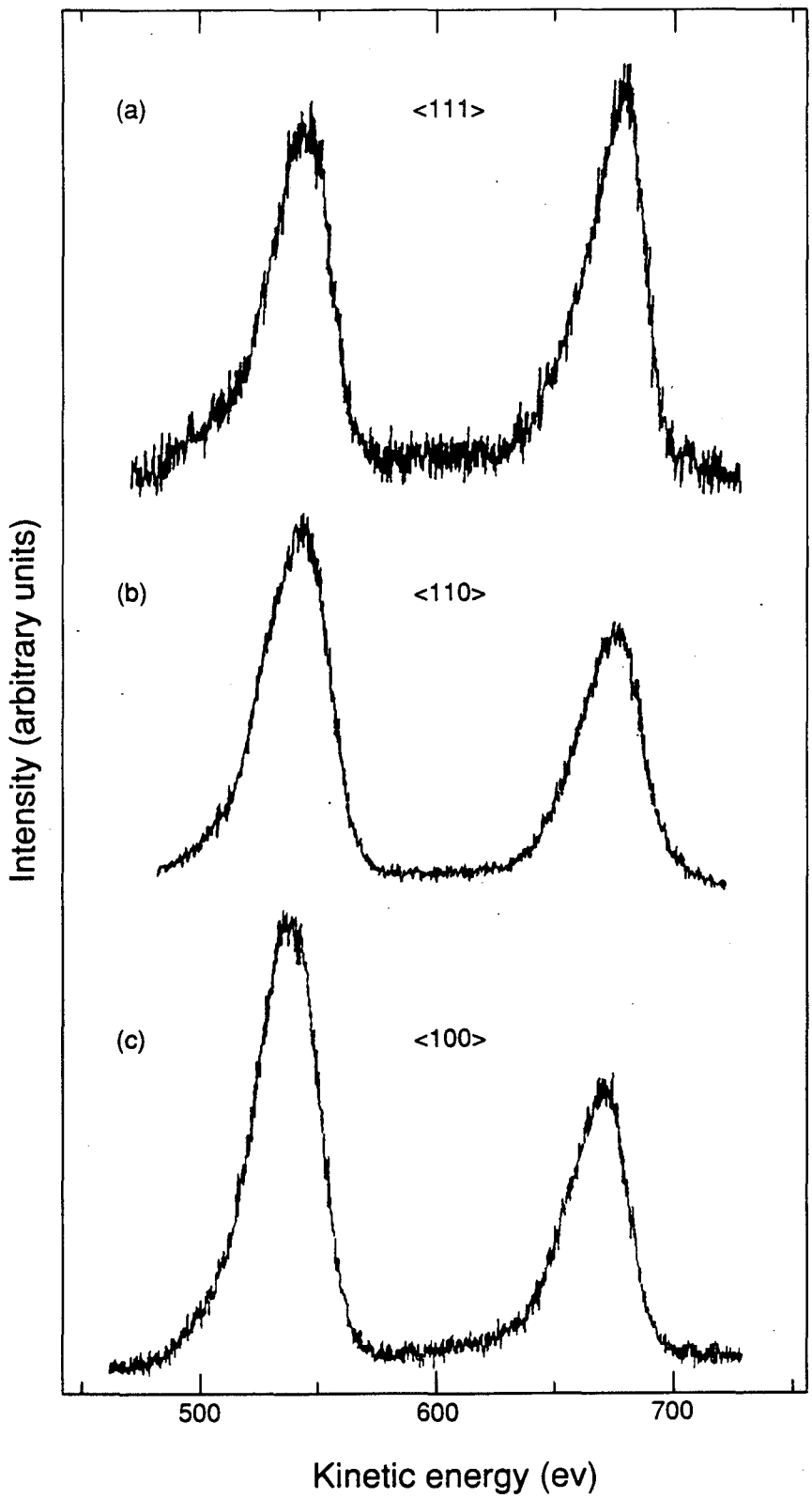


Fig. 1

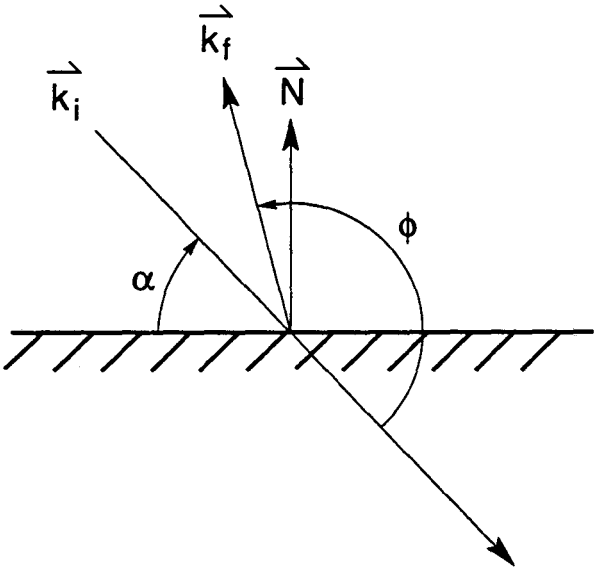
XBB 899-7779A



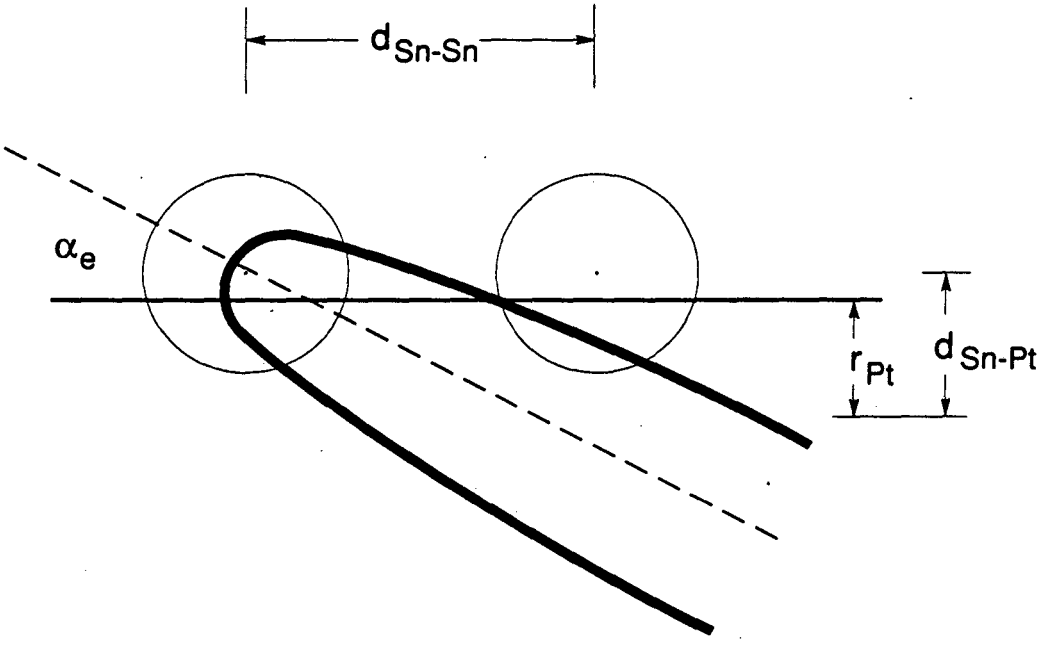
XBL 905 – 6400

Fig. 2

(a)



(b)



XBL 907-2586

Fig. 3

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